46th Annual Composites, Materials, and Structures

Analysis of Pyrolysis Products from Ablative TPS

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Outline

1) Goals of pyrolysis studies.

2) Quantitative vs. Qualitative Gas Measurements.

3) PICA-NuSil background.

4) PICA-NuSil chemistry under ambient conditions.

5) PICA-NuSil chemistry at elevated temperature.

Pyrolysis Gas Measurement Goals

1) Glean insight into the decomposition mechanisms of TPS materials.

2) Derive molar yields of gas phase products as a function of temperature and heating rate.

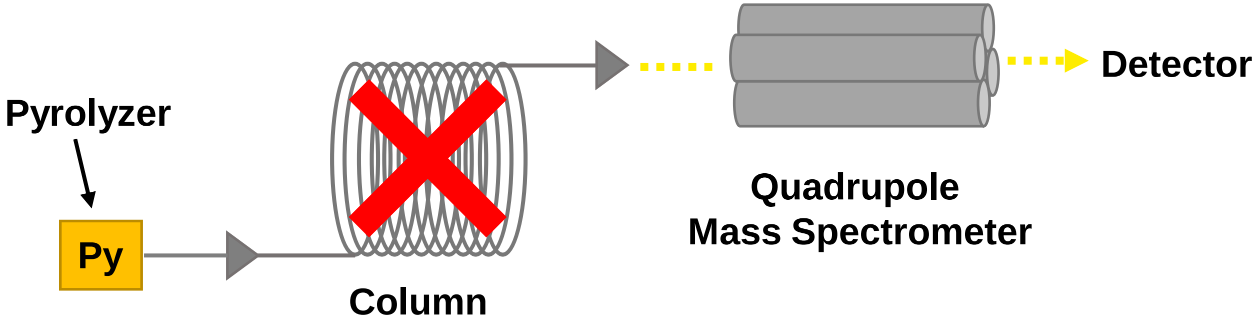
3) Guide and inform the development of material response models.

Pyrolysis Gas Measurements

Commercial Systems

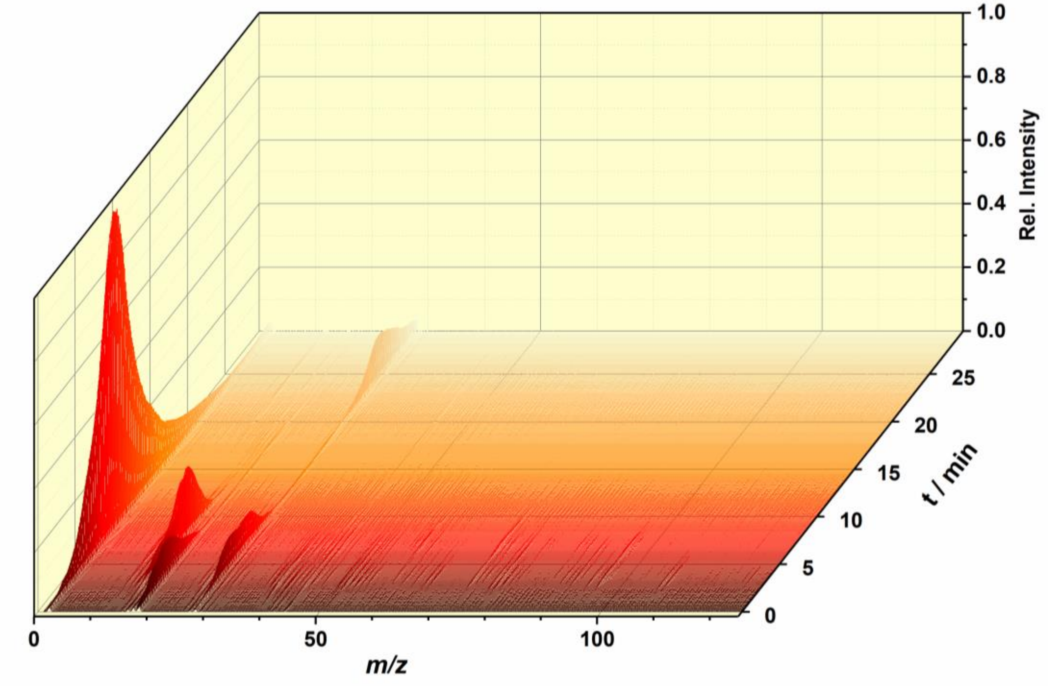
1) Pyrolysis Gas-Chromatography Mass-Spectrometry

2) Thermogravimetric Analysis Mass-Spectrometry

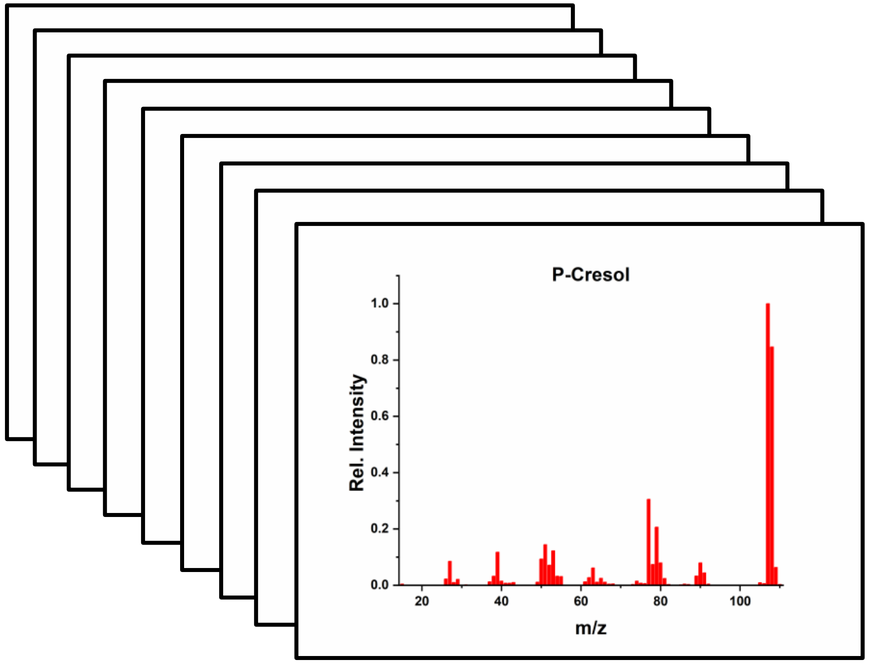


Pyrolysis Gas Analysis

M.S. Waterfall Plot



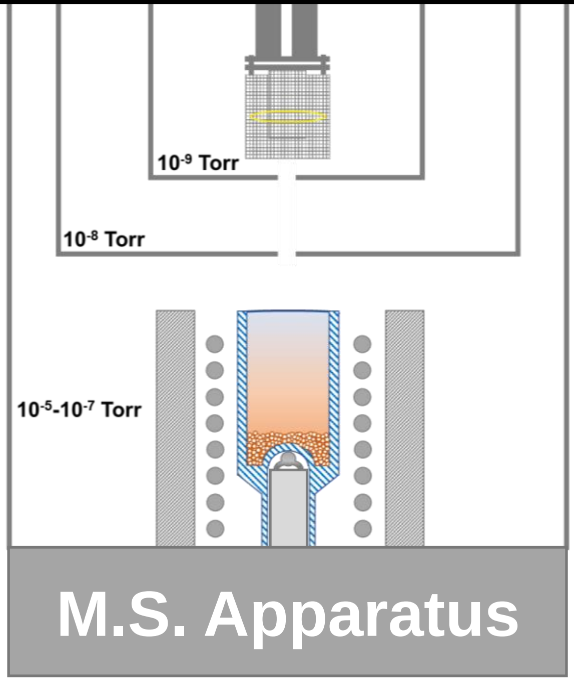
Mass Spectrum Library



- Raw mass spectra a fit with a linear combination of reference mass spectra to obtain coefficients for individual species.
- Detection sensitivity of the mass spectrometer needs to be accounted for.

$$[A]^{-1}\,[R] = [P]$$

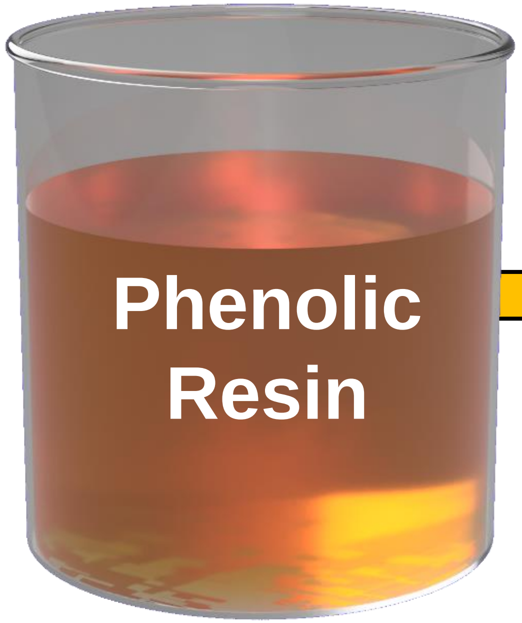
Pyrolysis Gas Analysis

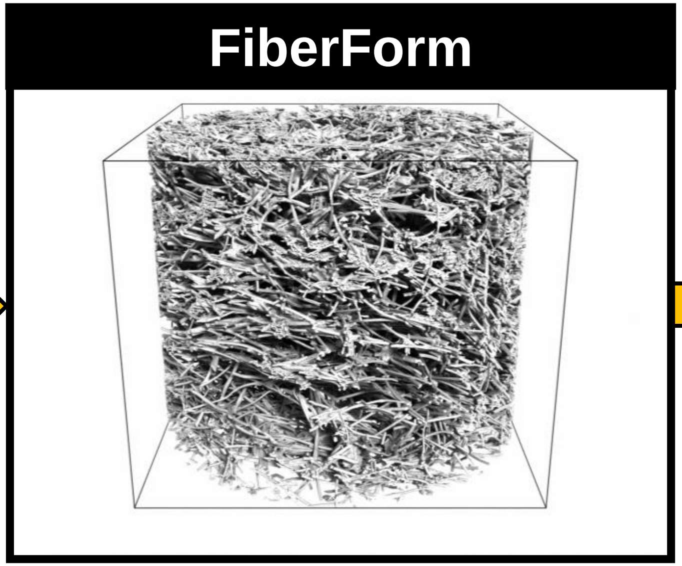


- Spectrometer detection sensitivities are a product of:
  - Ionization efficiency of the electron-impact ionizer
  - Transmission efficiency of the quadrupole
  - Gain in the ion detector

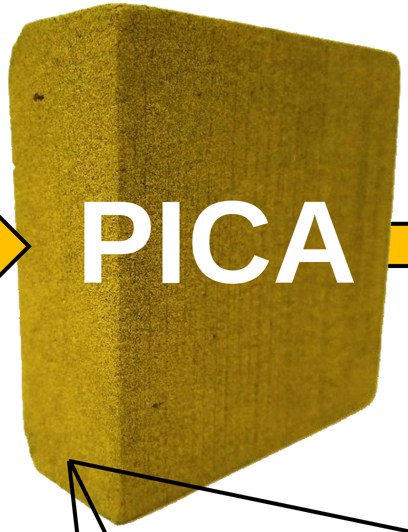
What is PICA-NuSil?

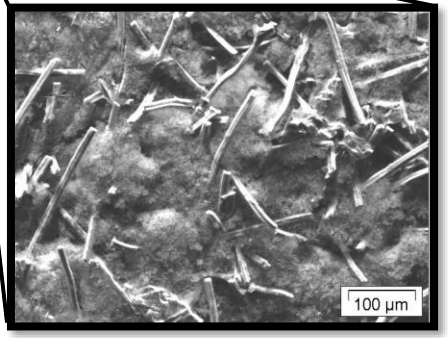
Phenolic Impregnated Carbon Ablator





Panerai, F. Int. J. Heat Mass Transfer 2017, 108, 801-811





SEM Images: Lawson, J. W., Stackpoole, M. W., Shklover, V., NASA Technical Reports Server Report # ARC-E-DAA-TN1167

- MSL Heat Shield

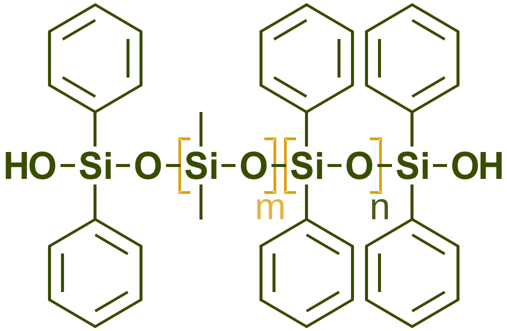
- PICA - created by NASA at Ames Research Center 1995

- Manufactured by impregnating a carbon fiber preform with phenolic resin.

NuSil (CV-1144-0)

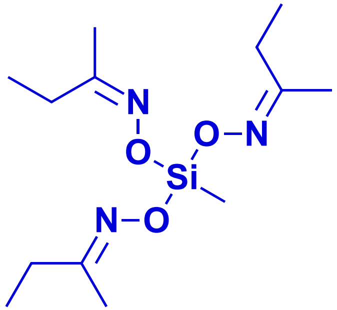
- CV-1144-0 is a single-component RTV dispersion in VM&P Naphtha.
- Polymerization initiates upon contact with atmospheric moisture.
- Polymer is end-capped by hydroxyl functional groups and either phenyl or methyl groups.
- Primary Use (EDL) : Sprayed on the surface of flight hardware to mitigate the shedding of phenolic particulate during ATLO.

Siloxane Copolymer Backbone



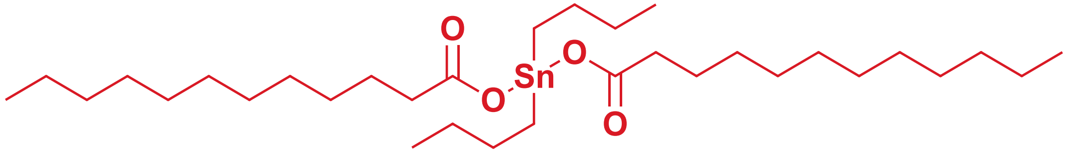
m = 0.95 ; n = 0.05

Oxime Crosslinking Agent

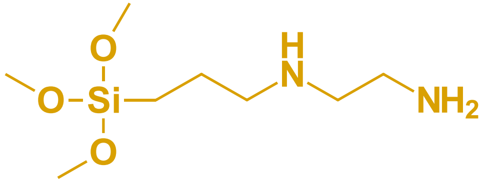


5-10 wt. %

Tin Catalyst



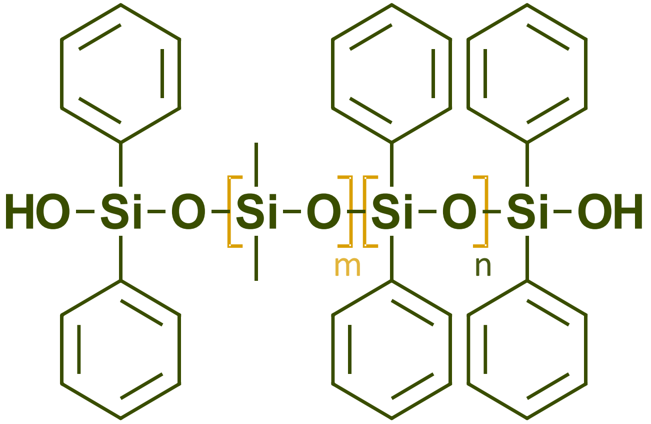
Siloxane Coupling Agent



PICA + NuSil

+

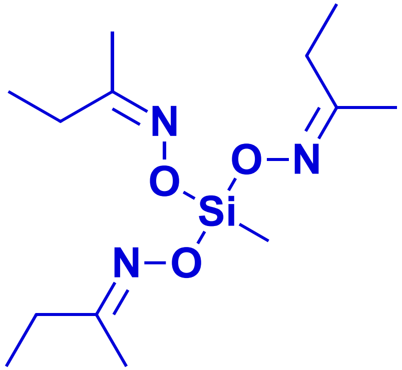
Siloxane Copolymer Backbone



m = 0.95 ; n = 0.05

+

Oxime Crosslinking Agent

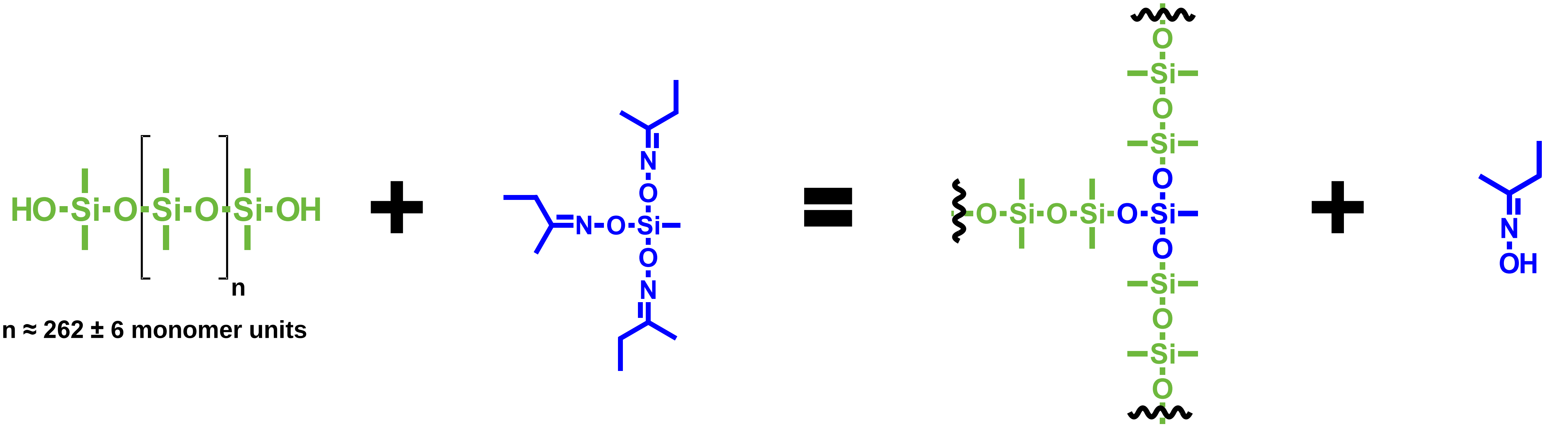


= ?

Do components of NuSil react with PICA?

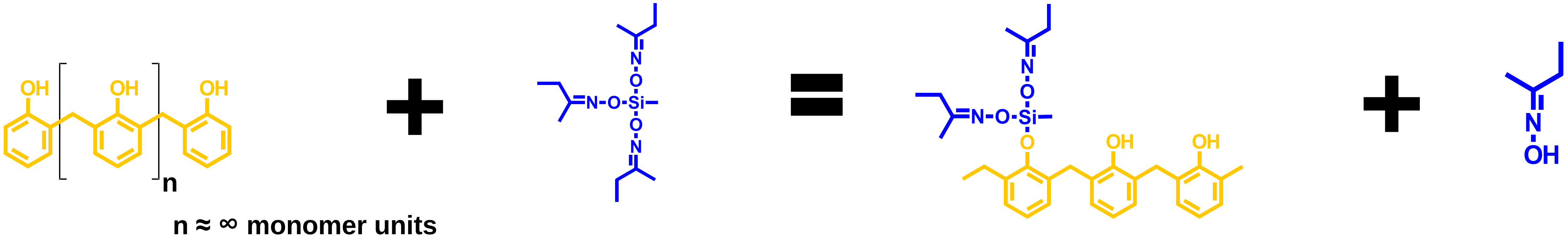
Possible Reactions Under Ambient Conditions

1A) Crosslinking compounds reacts with hydroxyl groups of siloxane in NuSil.

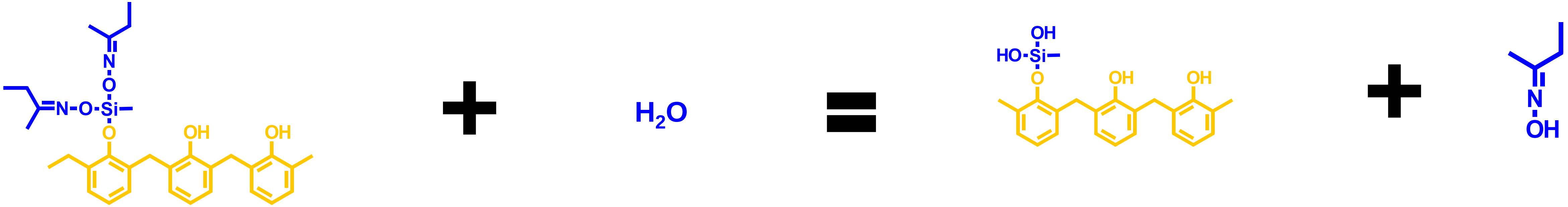


Possible Reactions Under Ambient Conditions

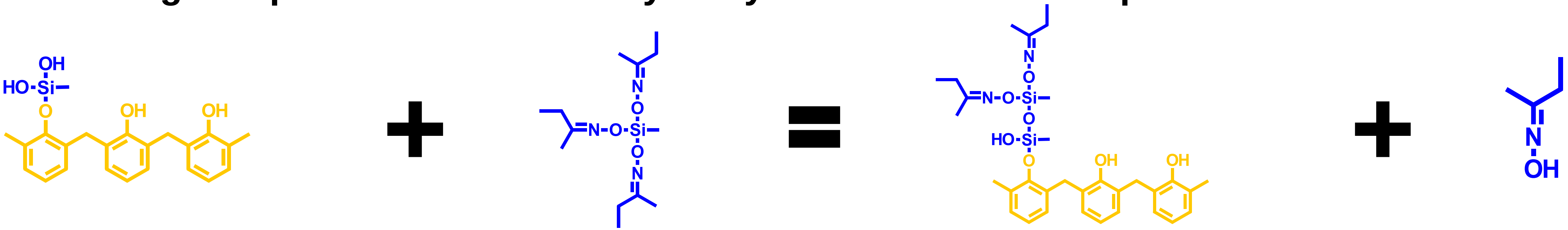
1B) Crosslinking compounds reacts with hydroxyl functional units of phenolic resin.



2B) Crosslinking compounds reacts with hydroxyl functional units of phenolic resin.

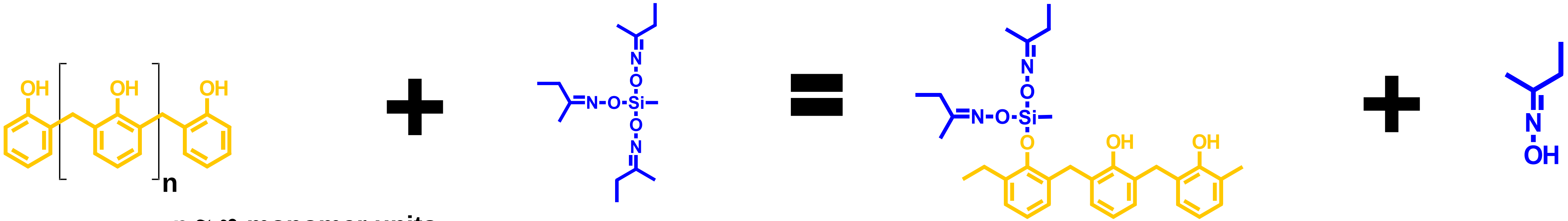


3B) Crosslinking compounds reacts with hydroxyl functional units of phenolic resin.



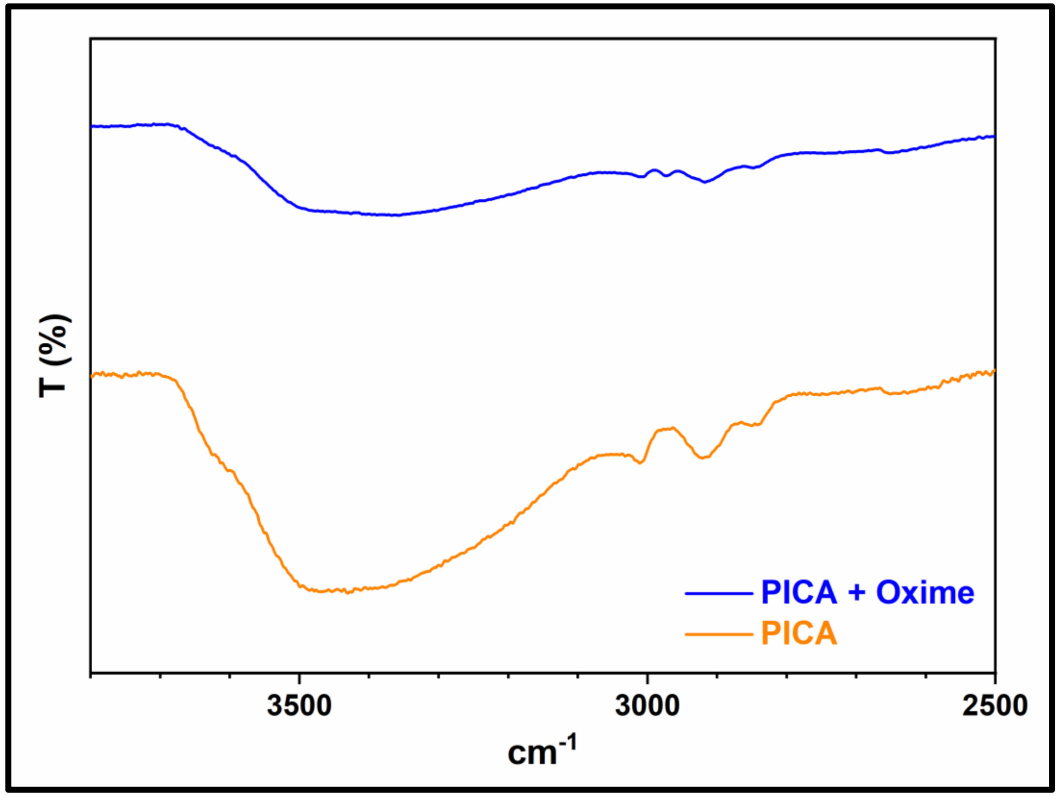
Possible Reactions Under Ambient Conditions

1B) Crosslinking compounds reacts with hydroxyl functional units of phenolic resin.



n ≈ ∞ monomer units

- **5 wt. % oxime mixed with naphtha.**
- **2 mm. dia. rod of PICA soaked in solution overnight.**
- **PICA + oxime cured in open air for 1 week.**
- **Attenuated Total Reflectance (ATR) spectra reveal a decreased intensity of OH stretch (3000 cm^{-1} – 3550 cm^{-1}).**



Thermal Decomposition Studies of PICA - NuSil

A) Crosslinker (Oxime)

- Poured into beaker and cured at room temperature for one week.

B) NuSil

- Poured into beaker and cured at room temperature for one week.

C) PICA

- Stored in open air.

D) PICA + 5 wt. % Oxime

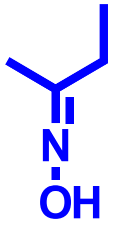
- Mixed 5 wt. % of oxime with naphtha.
- 2 mm dia. rod of PICA soaked in oxime solution overnight.
- PICA + oxime cured in open air for 1 week.

E) PICA + 45 wt. % NuSil

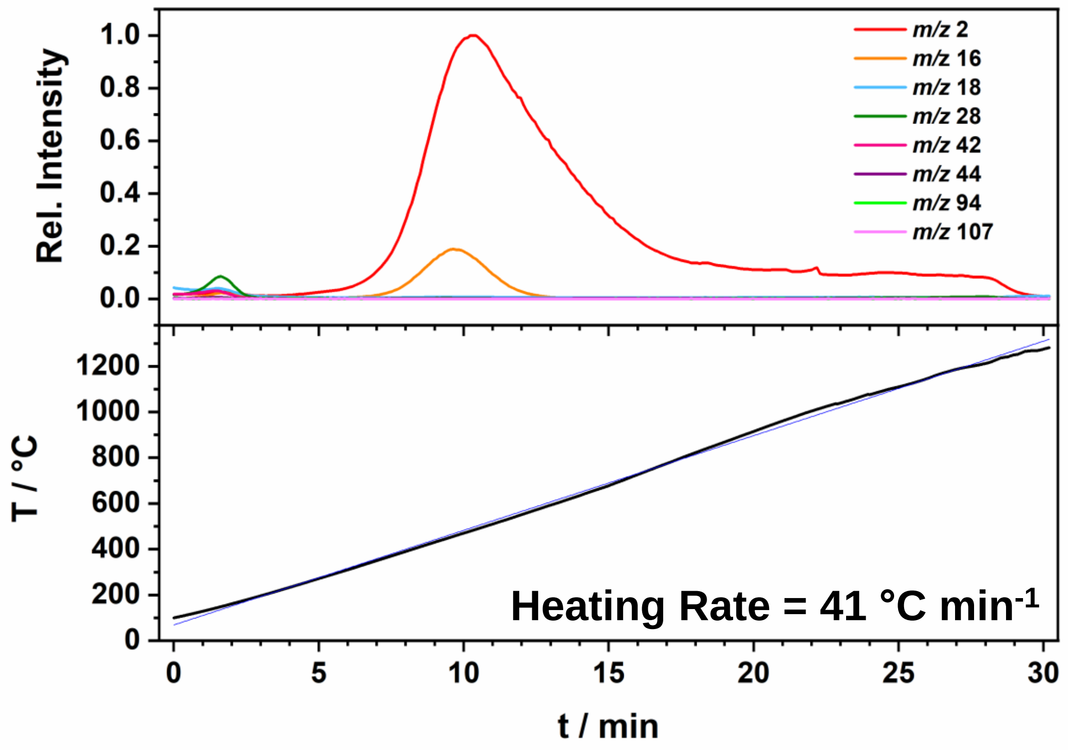
- Mixed 45 wt. % of NuSil with naphtha.
- 2 mm dia. rod of PICA soaked in NuSil solution overnight.
- PICA + NuSil solution cured in open air for 1 week.

A) Crosslinking Compound

- **Dominant pyrolysis products:**
  - **H_2 & CH_4.**
  - ***m/z* 2 – peak evolution at 485 °C.**
  - ***m/z* 16 – peak evolution at 457 °C (9.7 min).**
  - ***m/z* 28 – peak evolution at 149 °C.**
  - ***m/z* 42 – peak evolution at 142 °C.**



Thermal Decomposition of Oxime

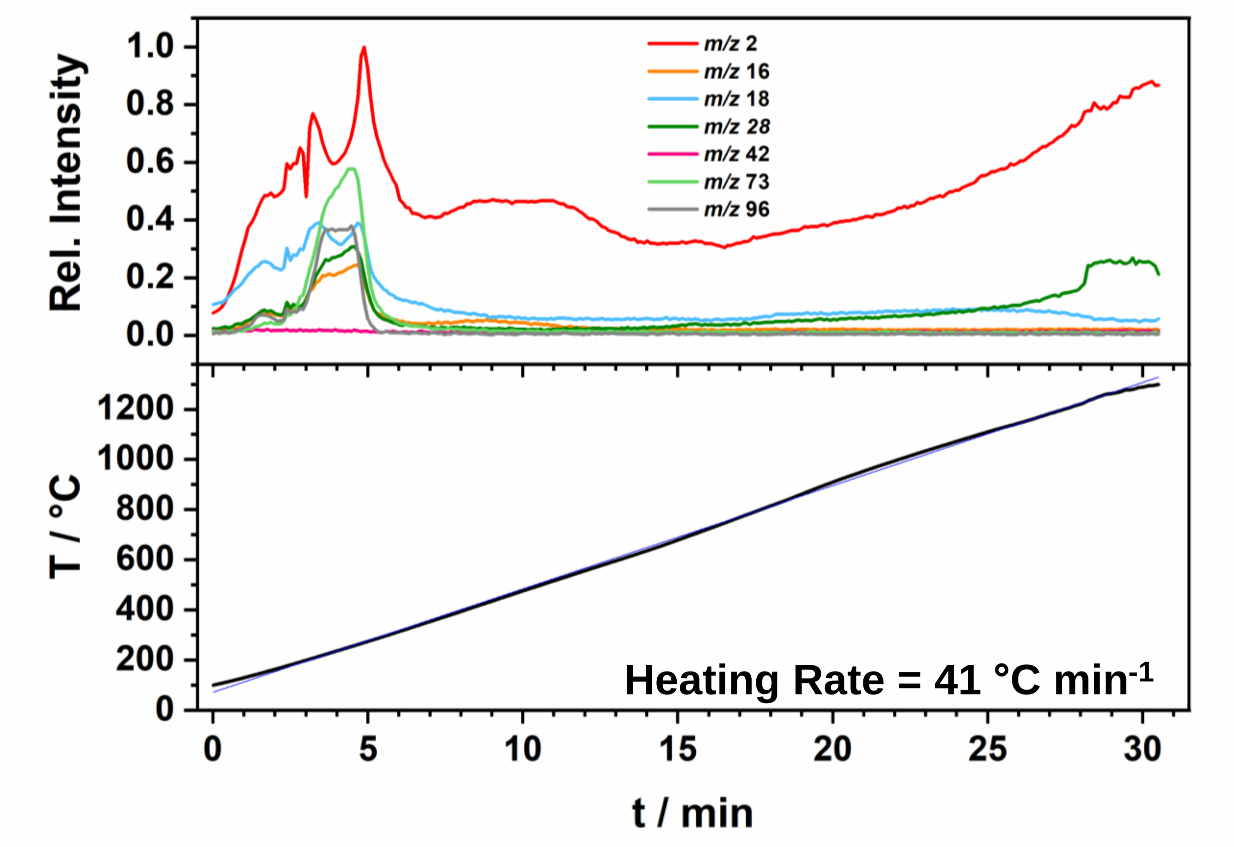


- **Mass spectrometer and TGA data suggest that the crosslinking agent polymerizes with itself and is table at high temperatures.**
- **Char yield ~ 60 wt. % at 1,200 °C.**

B) NuSil

- **Dominant pyrolysis products:**
  - **H_2, CH_4, H_2O, CO, & siloxane oligomers.**
  - ***m/z* 16 – two peaks centered at 238 °C and 433 °C (9 min).**
  - ***m/z* 28 – two peaks centered at 238 °C and 1,230 °C.**
    - **Polymer backbone fragments appear between 175 °C and 294 °C.**
      - ***m/z* 73 – daughter fragment of octamethyltrisiloxane.**
      - ***m/z* 96 – daughter fragment of hexamethylcyclotrisiloxane.**

Thermal Decomposition of NuSil



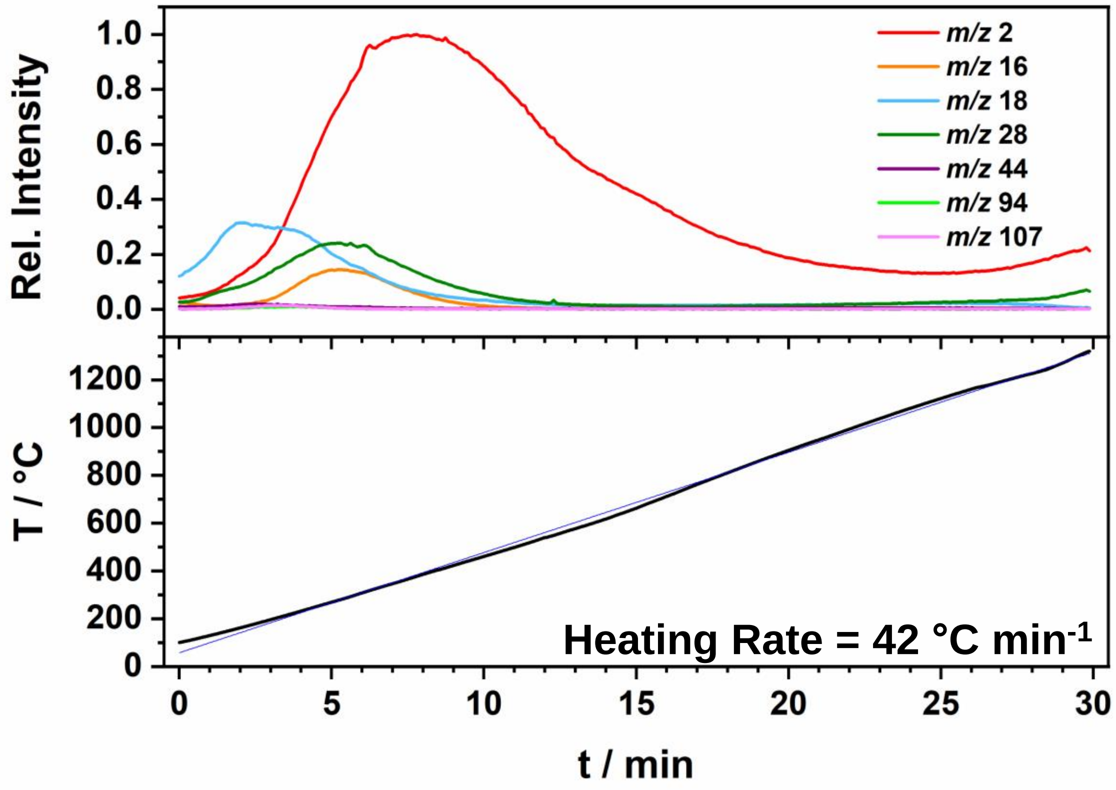
- **Polymer backbone fragments appear between 175 °C and 294 °C.**

- **The char yield of NuSil is ~ 10 wt. % at 1,200 °C.**

C) PICA

- **Dominant pyrolysis products:**
  - **H_2, CH_4, H_2O, CO.**
  - **Signal from polymer backbone fragments (e.g., phenol, cresol).**
  - **m/z 18 – Water evolves as a product of ether bond formation between hydroxyl functional groups of the phenolic polymer.**
  - **m/z 16, 28 – Peak evolution of methane and carbon monoxide at <u>t ≈ 5.5 minutes</u>.**
  - **m/z 2 – Peak evolution of Hydrogen at 7.7 min.**
  - **m/z 2, 28 – Hydrogen and Carbon Monoxide rise again after T > 1,100 °C.**

Thermal Decomposition of PICA

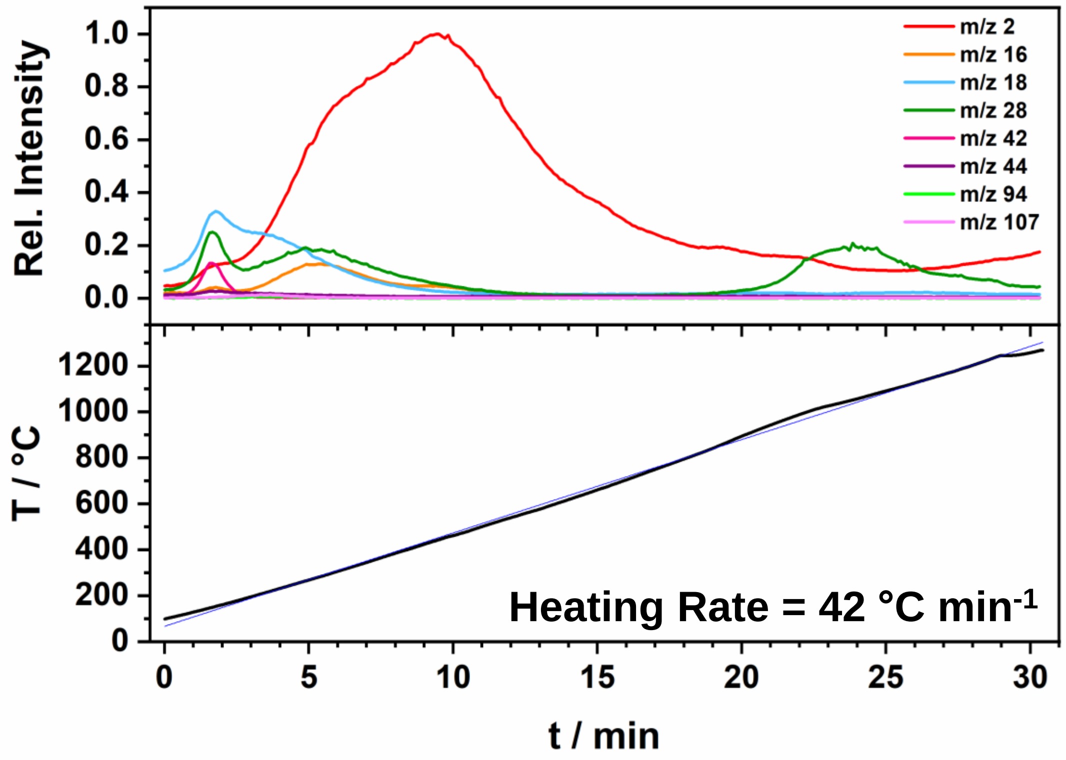


- **Char yield typically 80 wt. %.**

D) PICA + 5 wt. % Oxime

- **Dominant pyrolysis products:**
  - **H_2, CH_4, H_2O, CO, 2-butanone oxime (*m/z* 42).**
  - ***m/z* 18 – Low temperature evolution of water is bimodal. Second peak is lower and may be attributed to reaction between hydroxyl groups of phenol and oxime.**
  - ***m/z* 2, 16 – Evolution of hydrogen and methane are bimodal.**
  - ***m/z* 28 – Evolution of carbon monoxide at low and high temperature.**
  - **Evolution of carbon monoxide may be attributed to localized carbothermal reduction.**

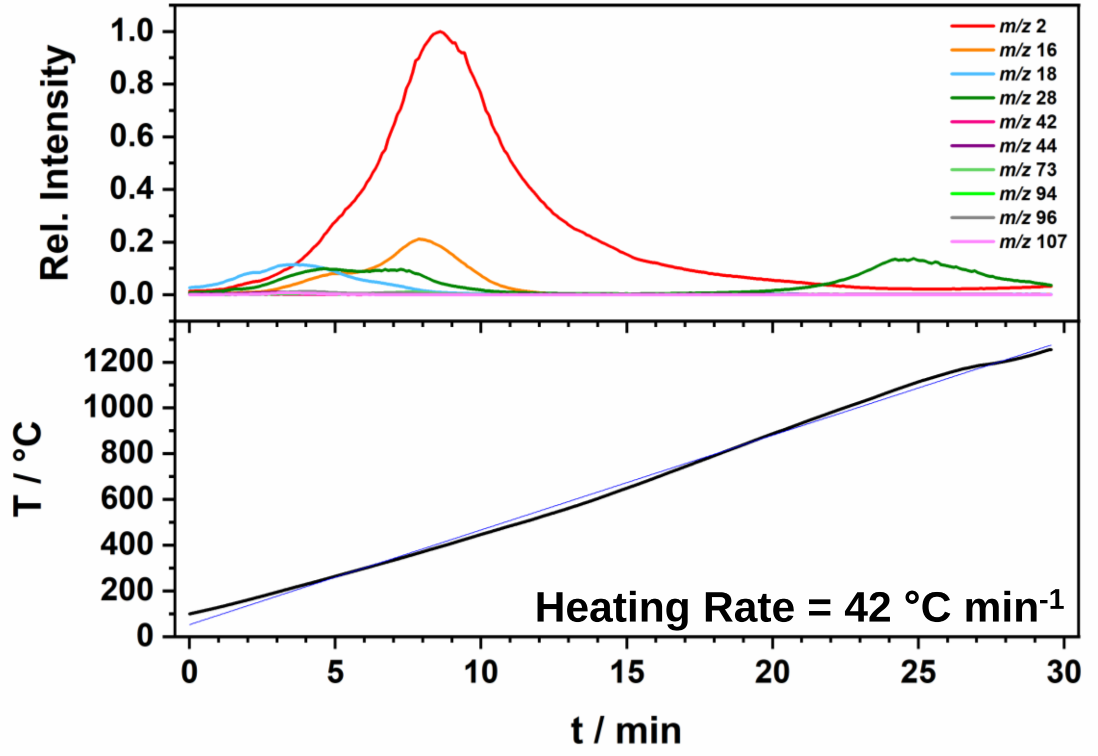
Thermal Decomposition of PICA + Oxime



E) PICA + 45 wt. % NuSil

- **Dominant pyrolysis products:**
  - **H_2, CH_4, H_2O, CO.**
  - ***m/z* 18 – Low temperature evolution of water is bimodal. Evolution of water may be reduced in the presence of NuSil.**
  - ***m/z* 2, 16 – Evolution of hydrogen and methane are bimodal. Peak methane production is shifted to higher temperature.**
  - ***m/z* 28 – Evolution of carbon monoxide at low and high temperature.**

Thermal Decomposition of PICA + NuSil



Conclusions

- **Oxime crosslinking unit reacts with PICA under ambient conditions.**
- **Oxime and NuSil react with PICA at high-temperature.**
- **NuSil increases the concentration of methane relative to PICA.**
- **It is suspected that the siloxane resin and the oxime crosslinker decompose at relatively low temperatures to form amorphous silicon oxycarbide materials.**
- **The high-temperature formation of carbon monoxide may result from reactions between localized silica and carbon.**

END

Questions